Regenerable sorbents for mercury capture in simulated coal combustion flue gas

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Abstract

This work demonstrates that regenerable sorbents containing nano-particles of gold dispersed on an activated carbon are efficient and long-life materials for capturing mercury species from coal combustion flue gases. These sorbents can be used in such a way that the high investment entailed in their preparation will be compensated for by the recovery of all valuable materials. The characteristics of the support and dispersion of gold in the carbon surface influence the efficiency and lifetime of the sorbents. The main factor that determines the retention of mercury and the regeneration of the sorbent is the presence of reactive gases that enhance mercury retention capacity. The capture of mercury is a consequence of two mechanisms: (i) the retention of elemental mercury by amalgamation with gold and (ii) the retention of oxidized mercury on the activated carbon support. These sorbents were specifically designed for retaining the mercury remaining in gas phase after the desulfurization units in coal power plants.

Keywords: mercury, gold, coal combustion, regeneration

1. Introduction

The environmental and health consequences of exposure to toxic mercury species are a matter of great concern. [1-2]. Governments, organizations and scientists worldwide devote significant efforts to prevent mercury pollution [3-6]. However, it was not until January 2013 that more than 140 nations adopted the first legally-binding international treaty aimed at reducing anthropogenic mercury [7].

Coal combustion constitutes one of the main sources of mercury emissions [8], representing 24% of global anthropogenic [9]. Mercury released from coal during combustion in power plants may be present in three forms: elemental mercury ($Hg^0(g)$), oxidized mercury ($Hg^{2+}(g)$) and particulate-associated mercury (Hg^P). Hg^P and $Hg^{2+}(g)$ can be retained in particle control devices and gas cleaning systems (e.g. flue gas desulphurization, FGD) units. However, $Hg^0(g)$ is a species that is more difficult to capture.

Mercury emissions from coal combustion can be controlled by pre-combustion and post-combustion strategies. Pre-combustion not only involves preparing coal blends or cleaning the coal to reduce the amount of mercury in the combustible [10], but also adding reactants, such as bromides, which produce reactive mercury species in the gases that can easily react or be adsorbed by the sub-products [11]. Post-combustion technologies are mainly based on sorbents that are generally injected into the gaseous stream and subsequently retained in particulate control devices [12-13]. Although field tests have been relatively successful, several aspects such as the amount of carbon to be injected, sorbent costs, implications for the fly ashes or effects on the operation of the plant, still require further investigation [14-15].

Hg^0 is the most difficult species to retain and requires a specially adapted retention method. A reliable method of Hg^0 capture would be to exploit the tendency of

this species to amalgamate with metals [16-18]. The flue gas from coal combustion could be passed over a metal-loaded material where the Hg^0 would amalgamate. The amalgam-containing sorbent could then be recycled in order for the mercury and the raw material to be recovered. The MerCap™ (Mercury Control Adsorption Process) project [19] is based on this concept. It consists in placing gold-coated metal structures into a flue gas stream to amalgamate the mercury and then thermally regenerating the sorbent, so as to recover the mercury. The drawback to this technology is that large amounts of gold are needed to coat the support. This problem could be reduced if sorbents, containing minimal amounts of gold are developed [19-21]. The present study explores the capacity of an activated carbon loaded with gold dispersed nano-particles, prepared in a previous work [22], to act as a sorbent for mercury. The carbon gold-loaded materials were developed to be used at the end of the coal combustion cycle, where the species of mercury in the outgoing gases will be mainly Hg^0 as most of the oxidized mercury will have already been retained in the particle control devices and desulfurization plants.

The main objectives of this study were to determine the effectiveness of these sorbents for mercury retention as well as the effect of multiple regeneration cycles on their lifetime and to evaluate the effect of acid gases upon the performance of the sorbent. This work also lays the foundation for developing procedures to recover other valuable products present in the used up sorbents and offers a tentative economic analysis.

2. Experimental

Gold-loaded carbon sorbents (Au-RB3) were prepared by the tetrakis (hydroxymethyl)phosphonium chloride (THPC) method which is based on the

107 formation of gold colloids [22]. The support was a commercial activated carbon (Norit
108 RB3). The Au coating was almost 100% effective with THPC, which acts both as a
109 reducing agent and as an inhibitor of large particle formation. The carbon support was
110 impregnated with 0.1 and 5 wt% of gold to obtain two sorbents labelled Au0.1-RB3 and
111 Au5-RB3, respectively. The support was ground to a size of 0.2-0.5 mm before
112 impregnation.

113 A schematic diagram of the experimental device employed to retain and to
114 recover the Hg^0 for sorbent regeneration is shown in Figure 1. The fixed sorbent bed
115 (80.0 mg) is placed in a glass reactor where it is kept at a temperature of 40ºC. This is
116 the usual temperature of a flue gas stream at the exit of desulphurization plants.
117 Elemental mercury in gas phase (100 $\mu g\ m^{-3}$), obtained by means of a permeation tube,
118 was passed through the sorbent at 0.5 L min^{-1}. A simulated flue gas (SFG) consisting of
119 N_2 with 6% O_2, 135 mg Nm^{-3} SO_2, 100 mg Nm^{-3} NO, 25 mg Nm^{-3} HCl, 16% CO_2 and
120 3% H_2O was employed as carrier gas. The temperature of the gas was maintained at
121 120ºC. Regenerable sorbents were developed for use after the DeNOx, particle control
122 devices and desulphurisation units (i.e., in an atmosphere relatively free of acid gases).
123 For this reason the composition of the gas was similar to what one might expect to find
124 just before the stack in a coal combustion power plant (i.e., with a low sulphur, halogen
125 and nitrogen species content). The results were compared with those obtained in an
126 atmosphere of N_2 and O_2, SO_2 or HCl in N_2 in proportions identical to those in the SFG
127 atmosphere. The Hg^0 not retained in the sorbents was measured using a continuous
128 mercury monitor (VM-3000). The mercury content of the sorbent after retention was
129 determined by means of AMA equipment. The duration of each cycle of retention was 3
130 days.

131 The oxidation of mercury was evaluated by capturing the Hg^{2+} in an ion
132 exchanger resin (Dowex® 1x8). The resin was treated with a mixture of HCl:H_2O (1:1)
133 at 90ºC for 30 minutes. It was then placed at the exit of the reactor prior to the Hg^0
134 continuous analyzer ((1) in Figure 1). The Hg^{2+} in the resin was determined by AMA.
135 Atmospheres of O_2, SO_2, NO or HCl in N_2, and combinations of these gaseous species
136 were evaluated to assess the influence of each gas upon mercury speciation.
137 To evaluate the regeneration, the post-retention sorbents were heated in the same
138 experimental device from room temperature to 550 °C at a heating rate of 10ºC min^{-1}
139 under N_2. The desorbed mercury ((2) in Figure 1) was monitored as a function of
140 temperature using the VM3000 analyzer. The gold-doped regenerated sorbent was then
141 re-used to retain mercury. The experimental set-up was equipped with a device for the
142 recovery of Hg^0 ((3) in Figure 1). This device consists of a series of 44 tubes of 0.5x30
143 cm, arranged in rows of three and immersed in ice where Hg^0 is recovered and collected
144 in a container.
145 The gold was recovered by burning the Au-RB3 sorbent in a furnace at 700°C
146 under air to obtain a gold-containing residue. The metal was separated from the other
147 components of the residual ash by adding elemental mercury at a ratio of 2:1 (Hg:Au) to
148 form the Hg-Au amalgam. The suspension was maintained under stirring for 24h and
149 the amalgam was separated from the ashes by sieving (212 μm). The process was
150 repeated until the gold had been totally recovered. Finally, the mercury and gold were
151 separated by heating the amalgam to 450ºC. The mercury was collected in a container
152 ((3) in Figure 1) and the gold was recovered in the reactor.

153 **3. Results and discussion**

154 *3.1. Mercury retention*

155 *3.1.1. Effect of gold content*

156

157 In a previous work [22], the RB3 activated carbon was impregnated with
158 different amounts of gold (0.05-5 wt%), using the polyvinyl alcohol (PVA) and tetrakis
159 (hydroxymethyl) phosphonium chloride (THPC) methods. The quantities of mercury
160 retained in the sorbents prepared by these methods were similar for a given gold
161 content, but the THPC was the more efficient for loading the gold. When freshly
162 prepared sorbents are used, even the samples with only 0.1wt % of gold had a mercury
163 retention capacity and efficiency comparable to that of the commercial activated carbon
164 RBHG3 [22], which is specifically designed for mercury retention at low temperatures.
165 However, RBHG3 is not regenerable. These promising results led us to investigate
166 whether these sorbents are regenerable and maintain their good retention properties after
167 several cycles.

168 Figure 2 shows the mercury breakdown curves for the sorbent with the lowest
169 gold content (Au0.1-RB3), over three regeneration cycles under N_2 and O_2+N_2
170 atmospheres. The presence of O_2 (12.6 vol%), did not have any significant effect on
171 mercury retention since the results were similar to those in the inert atmosphere. What is
172 remarkable is that mercury retention decreased sharply after the first cycle of
173 regeneration. After 3 days, the mercury retention capacity of the fresh Au0.1-RB3
174 sorbent achieved retention values of 2.5±0.3 mg g^{-1} with an efficiency of 100% for more
175 than 24 hours and maximum retention capacity was still not reached even after 3 days.
176 With the second cycle, mercury capture decreased to 0.4±0.1 mg g^{-1}, remaining constant
177 thereafter over successive cycles of regeneration. In the case of the sorbent loaded with
178 5% gold (Au5-RB3), the qualitative behaviour was similar, but the quantity of mercury
179 retained after regeneration was considerably higher (Figure 3). In this case, the mercury

retention capacity reached values similar to those of Au0.1-RB3 (2.3±0.2 mg g^{-1}) during the first cycle with 100% efficiency for approximately 1700 minutes, but in subsequent cycles, the mercury retention capacity remained constant at 1.1±0.2 mg g^{-1}. It should be noted that the amount of mercury retained over successive cycles was about 3 times higher in the sample loaded with 5% gold than in that loaded with 50 times less gold (0.1%). Therefore, increasing the amount of gold improves the performance of the sorbent but not in a directly proportional way. Nevertheless, the regenerated sorbent loaded with 5% gold fulfills the objectives. On the one hand, a high retention capacity was attained and, on the other, maximum retention capacity was reached after an acceptable breakdown time with 100% efficiency.

The different performances observed after the first cycle of retention may have been due to the degradation of the support or to degradation of the loaded gold. Theoretically, changes in the characteristics of the gold particles after the evaporation of mercury should not occur, especially in the case of Au5-RB3. The Au-Hg phase diagram reported by Okamoto and Massalski [23] (Figure 4), shows the path of mercury desorption in the sorbents. The Au/Hg ratio in the amalgam was 71/29 and 96/4 for Au0.1-RB3 and Au5-RB3, respectively. During the regeneration of Au0.1-RB3 the amalgam went through different solid phases until the mercury had been completely desorbed at 450 °C, but during the regeneration of Au5-RB3 the amalgam remained in the same solid phase (Figure 4). No changes in the morphology of the gold deposited on the sorbent before and after desorption (as observed by TEM) or in the oxidation state of the gold (as identified by XPS) were observed.

Possible modifications of the characteristics of the activated carbon support between cycles were also considered, and it was concluded that the different behaviour after the first and subsequent cycles was due to the presence of chlorine in the fresh

sorbent which evaporated after the first regeneration. The Au-loaded RB3 sorbents, prepared by impregnation using gold chloride [22], contain a small and slightly variable amount of chlorine (<15%) that may affect mercury capture on carbonaceous materials [24]. This explains the decrease in the retention of mercury after the first regeneration (Figures 2-3), since after regeneration at 550°C all the chloride is desorbed. In conclusion, when the Hg^0 in gas phase passes through the sorbent, some of the mercury remains as Hg^0 which is retained by amalgamation, while some is oxidized on the support in the presence of chlorine to form Hg^{2+} which is retained in the carbon support. When the sorbent loses the chlorine after the first regeneration, amalgamation is the only capture mechanism. Figure 5 shows the mercury desorption curves of Au5-RB3 after successive cycles of regeneration in N_2. The amount of Hg^0 desorbed during the first cycle, as determined by VM3000, is lower than the total amount of mercury retained in the sorbent, as analyzed by AMA. However, with the second cycle the amounts of mercury desorbed and retained are similar which confirms that, during the first cycle, mercury is oxidized and retained as Hg^0 and Hg^{2+}, whereas during the second and successive cycles it is retained as Hg^0. Nevertheless, it is important to note that mercury retention remains constant over a large number of cycles, which makes the Au5-RB3 a promising material for mercury capture.

3.1.2. Effect of the gas composition

The literature data show that flue gas components, such as SO_2, can poison the gold, making it ineffective for mercury capture [25]. This needs to be taken into account when considering regenerable sorbents. In Figure 6(a) it can observed that the capture of mercury by Au5-RB3 in the presence of SO_2 is slightly lower than in the presence of N_2 and N_2+O_2, during the first cycle of retention (1.9±0.3 mg g^{-1}). However, no significant

differences between the two atmospheres (Figures 3 and 6(a)) are apparent in the subsequent cycles of retention (0.9±0.2 mg g^{-1}). Mercury capture after the first cycle is again lower than that achieved by the fresh sorbent. Although the time during which mercury is retained with 100% efficiency is shorter in the atmosphere of SO_2+N_2 than in that of O_2+N_2 during the first cycle, indicating that SO_2 might slightly reduce the effectiveness of gold-doped activated carbon, total poisoning of the gold does not occur, even after several cycles of regeneration (Figure 6(a)). A mercury retention capacity of the order of mg g^{-1} is still reached and maintained over several cycles. The influence of HCl on the adsorption of mercury by Au5-RB3 is shown in Figure 6(b). It can be seen that, unlike SO_2, HCl improves mercury capture. Indeed, after successive regeneration cycles the mercury retention capacity remains constant at 2.7 mg g^{-1} with an efficiency of 100% for more than 2000 minutes during every cycle. These results again suggest that Hg^0 may be oxidized in the sorbent, with retention being favored by the presence of HCl [26]. This would explain why retention is maintained over successive cycles in the presence of HCl but not in the case of O_2, N_2 and SO_2 (Figures 3 and 6(a)). In a previous study carried out by the authors [27] it was concluded that an atmosphere containing only HCl increased mercury retention considerably and promoted heterogeneous mercury oxidation in the presence of carbonaceous matter, which may have catalyzed the reaction between Hg and HCl [28]. Therefore, when HCl is present in the flue gas, mercury is retained as $HgCl_2$ in the carbonaceous support while the non-oxidized mercury is retained by the nano-dispersed gold throughout all the retention cycles.

Finally, mercury retention was evaluated in synthetic gas mixtures typical of coal combustion with and without water vapor in their composition. For comparison purposes Table 1 shows the mercury retention capacity recorded for Au5-RB3 in these

two atmospheres and that observed in the N_2 atmosphere. Also listed are the data obtained for the raw activated carbon without gold (RB3). Figure 7 shows the mercury adsorption curves for Au5-RB3 over several regeneration cycles under the two gas mixtures. In these reactive gas-containing atmospheres, the sorbent proved to be 100% efficient over successive cycles of utilization as when HCl was present in the flue gas. After successive regeneration cycles the mercury retention capacity remained constant at 2.9 mg g^{-1} with an efficiency of 100% for more than 4000 minutes during every cycle. The presence of H_2O does not seem to have any effect on mercury retention or regeneration (Figure 7(a)). However, when the mercury desorption curves corresponding to cycles of regeneration in N_2, SFG and SFG without H_2O, are compared (Figure 8), it can be seen that the peak temperatures differ. The desorption of mercury starts at approximately 120 ºC but its total decomposition does not occur until 280±20 ºC in N_2 and SFG. However, in SFG without H_2O the desorption of mercury shows two peaks with maxima at approximately 210 and 340ºC, which indicates that the species of mercury retained are different. From the results obtained for RB3 (Table 1), it can be seen that, whereas in N_2 mercury retention was very low, in SFG both with and without H_2O, it reached values of 0.6 and 1.5 mg g^{-1}, respectively, suggesting that mercury compounds may have formed as a result of homogeneous oxidation (gas-gas interactions) or interactions between the activated carbon and the gases (heterogeneous oxidation).

Figure 9 shows the percentages of Hg^0 and Hg^{2+} detected for each of the gas compositions studied. The results indicate that no homogeneous oxidation reactions occurred in the single gases O_2, SO_2 and HCl under the experimental conditions tested. However, in the NO atmosphere, approximately 28% Hg^{2+} was formed. When O_2 was present with SO_2 and NO, oxidation was 3 and 48%, respectively. This would suggest

that O_2 has a synergistic effect on mercury oxidation not only via SO_2 which is in agreement with the results of a previous study [27], but also and mainly via NO. When the other components were added to the gas composition (i.e., O_2+NO+SO_2+HCl+CO_2+N_2) the percentage of mercury oxidation was similar (around 40%) to that obtained with O_2+NO+N_2 (48%) (Figure 9), but it differed in the presence of H_2O. It can be deduced, therefore, that SO_2 in O_2, and mainly NO, with or without O_2, are the main gas combinations responsible for the homogeneous oxidation of mercury. The gas species might be HgO which would form through reactions (I-V).

$$Hg^0\,(g) + SO_2\,(g) + O_2\,(g) \rightarrow HgO\,(s,g) + SO_3\,(g) \qquad (I)$$

$$2\,Hg^0\,(g) + 2\,NO\,(g) \rightarrow 2\,HgO\,(s,g) + N_2\,(g) \qquad (II)$$

$$NO\,(g) + O_2 \rightarrow NO_2\,(g) + O \qquad (III)$$

$$Hg^0\,(g) + O \rightarrow HgO\,(g) \qquad (IV)$$

$$Hg^0\,(g) + NO_2\,(g) \rightarrow HgO\,(s,g) + NO\,(g) \qquad (V)$$

It is, however, remarkable that mercury oxidation decreased when H_2O was present in the gas (Figure 9). Oxygen has a positive effect on mercury oxidation but when both water vapor and oxygen coexist in the simulated flue gas the conversion of Hg^0 to Hg^{2+} may decrease due to competition between the O and OH, which would prevent the above reactions. It was found that a small amount of moisture may enhance oxidation (<0.74%) whereas a large amount (in this study 3%) may have the opposite effect [29].

The level of capture of the Hg^{2+} produced by homogeneous oxidation was evaluated using sorbent beds made up of RB3 and Au5-RB3. Figure 10 shows the

302 percentages of Hg^{2+} and Hg^0 in the outlet gas and the percentage of mercury retained in
303 the sorbent (Hg_P). The atmospheres employed were N_2 and the mixtures
304 O_2+NO+SO_2+HCl+CO_2+N_2 (SFG without water) and O_2+NO+SO_2+HCl+CO_2+H_2O
305 +N_2 (SFG with water). As can be observed in Figure 10(a), RB3 does not retain mercury
306 in the inert atmosphere. However, in the gas mixtures mercury was captured and a slight
307 amount of Hg^{2+} coming from the reactor was identified. In the SFG without water the
308 amount of Hg^{2+} outside the sorbent was around 2% compared to 34% Hg^{2+} resulting
309 from homogeneous oxidation (Figure 9). In the case of SFG only 1% Hg^{2+} was
310 collected at the exit of the reactor. This percentage was also lower than that produced by
311 homogeneous oxidation in this atmosphere (4%) (Figure 9). These results demonstrate
312 that most of the Hg^{2+} produced by homogeneous oxidation was retained in the RB3
313 sorbent. The mercury species formed after interaction with the sorbent Au5-RB3 are
314 shown in Figure 10(b). If we compare the percentages of the three species in RB3 and
315 Au5-RB3 important differences can be observed. In the N_2 atmosphere where there was
316 no homogeneous oxidation (Figure 9) and all the mercury is in the form of Hg^0, part of
317 the Hg^0 is retained, whereas the rest is released as Hg^0 (Figure 10(b)). As in the case of
318 RB3, in the atmosphere containing reactive gases, the amount of mercury oxidized at
319 the exit of the sorbent bed is minimal. As for RB3, most of the Hg^{2+} is retained in the
320 carbonaceous support in Au5-RB3. As might be expected, the main difference between
321 the results obtained with RB3 (Figure 10(a)) and Au5-RB3 (Figure 10(b)) is that no Hg^0
322 was detected at the exit of the reactor containing the Au5-RB3 sorbent since a 100%
323 efficiency was attained in both atmospheres.

324 We should also consider the possibility that, in addition to reactions (I-V), which
325 explain homogenous oxidation, the sorbent may act as a support for the formation of

326 $HgSO_4$ (reaction VI) [27] and/or different mercury nitrites and nitrates (reactions VII
327 and VIII) [30-32] in the SFG without water atmosphere.

328 $$Hg^0 (g) + SO_2 (g) + O_2 (g) \rightarrow HgSO_4 \quad (VI)$$

329 $$4\ Hg^0 (g) + 6\ NO (g) + 3\ O_2 (g) \rightarrow Hg_2(NO_3)_2 + Hg_2(NO_2)_2 + 2\ NO (g) \quad (VII)$$

330 $$4\ Hg^0 (g) + 4\ NO (g) + 3\ O_2 (g) \rightarrow Hg_2(NO_3)_2 + Hg_2(NO_2)_2 \quad (VIII)$$

331 In summary, the carbon material loaded with 5% gold (Au5-RB3) is able to
332 capture mercury with 100% efficiency in both O_2+NO+SO_2+HCl+CO_2+N_2 and
333 O_2+NO+SO_2+HCl+CO_2+H_2O+N_2 atmospheres over several cycles of regeneration. The
334 retention mechanism involves both the support and the gold. The RB3 support captures
335 Hg^{2+}, whereas the gold amalgamates Hg^0.
336
337 *3.2. Economic analysis*
338 *3.2.1 Gold recovery*
339 Although a procedure for recovering gold from the sorbent has not been
340 optimized in this work, a possible way of retrieving the gold used in the process would
341 be to separate the gold from the carbonaceous support by burning the organic matter.
342 Because the support (RB3 activated carbon) contains 6% of mineral matter, the key to
343 the process is to separate this mineral matter from the gold after combustion of the
344 carbon support. The separation would involve amalgamating the gold present in the
345 residue with the very same mercury recovered in the regeneration process. The global
346 process is, in fact, intended as a relatively re-established sequence. The gold recovered
347 in the first process of amalgamation with mercury was approximately 82% of the total.
348 The second amalgamation step increased the amount recovered 92% (Figure 11). This

amount could probably be improved upon by using successive amalgamation cycles but this must be the subject of a future study.

3.2.2 Cost analysis

The data obtained in this study were employed for a preliminary economic analysis (**y**) based on the cost of the sorbent, which mainly took into account the cost of the gold employed (**A**), the cost of the support (**B**) and the cost of preparing the sorbent (**C**). In this preliminary analysis, the expenses derived from the installation of the facility in the power plant were not included because at this stage (i.e., laboratory scale), any attempt to estimate the costs at industrial scale would be premature. It is also too early to evaluate the operating costs that would include the energy necessary for overcoming pressure drops and for producing the heat required for regeneration and maintenance. What follows therefore is an estimation of the investment required for the sorbent material.

The cost of the sorbent (**y**) will depend on the amount of sorbent (**m**) needed to retain all of the mercury emitted in gaseous phase.

Therefore

$$\mathbf{y = m\,(A + B + C)} \qquad (1)$$

where y is the cost in dollars ($) and m is the mass of sorbent (kg).

A simple relationship can be established between the amount of sorbent and the concentration of mercury in the gas phase, the breakthrough time, defined as the time during which the sorbent retains the mercury with 100% efficiency, and the retention capacity of the sorbent. This relationship can be expressed as:

$$\mathbf{m} = \frac{Q \cdot C \cdot tb}{RC} \qquad (2)$$

where Q is the flow rate ($m^3\ h^{-1}$), C is the mercury concentration ($\mu g\ m^{-3}$), t_b is the breakthrough time (h) and RC is the mercury retention capacity ($\mu g\ Hg^0\ kg^{-1}$ sorbent).

The cost of the gold employed (**A)** can be estimated as:

$$\mathbf{A} = 0.05 \cdot Cg \qquad (3)$$

where 0.05 is the mass of gold per unit of mass of the sorbent Au5-RB3 ($gAu\ kg^{-1}$ sorbent) and Cg is cost of the gold per unit mass ($\$\ kg^{-1}$ Au).

The cost of the support (**B**) is calculated as:

$$\mathbf{B} = Cs \qquad (4)$$

where Cs is the cost of the support ($\$\ kg^{-1}$ support ~ $\$\ kg^{-1}$ sorbent).

Finally, the cost of preparation (**C**) is estimated as:

$$\mathbf{C} = 40.9 + 8044 \cdot H \qquad (5)$$

where 40.9 is the cost of the reagents per unit of sorbent ($\$\ kg^{-1}$ sorbent), 8044 is the cost of the energy employed per unit of sorbent ($kW{\cdot}h\ kg^{-1}$ sorbent) and H the cost of $kW{\cdot}h$ ($\$\ kW^{-1}{\cdot}h^{-1}$)

Therefore:

$$\mathbf{y} = \mathbf{m}\ (0.05 \cdot Cg + Cs + 40.9 + 8044 \cdot H\ ) \qquad (6)$$

This analysis was carried out assuming that the sorbent Au5-RB3 is able to retain mercury with an efficiency of 100% for at least three days, which represents in our experiment a mercury retention capacity of 2.9 mg g^{-1} in a simulated coal combustion flue gas. If this type of sorbent were employed in a 1200 MW pulverized coal combustion power station equipped with a flue gas desulphurization unit, and a mercury concentration of 8.6 $\mu g\ m^{-3}$ were produced with a flow rate of 131147 m^3/h, the amount of sorbent required for the complete retention of the emitted mercury would be approximately 28 kg**.** This would imply a total sorbent cost of approximately 126000$, as is shown in Table 2. However, this would be the initial investment. The recovery of

399 the gold for this or other applications would considerably make up for the cost of the
400 regenerable sorbent used in the plant.
401
402 **4. Conclusions**
403 A regenerable sorbent prepared by the dispersion of gold nanoparticles on a
404 carbon material using 5% doped gold was found to be highly effective for mercury
405 capture, exhibiting a 100% efficiency over several cycles of regeneration. The activated
406 carbon loaded with gold was able to retain Hg^{2+} on its own carbonaceous support in the
407 presence of chloride and Hg^0 by amalgamation with the noble metal. The sorbent was
408 thermally regenerated at approximately 240 ºC and the Hg^0 was recovered and collected
409 in a container. Although a high level of investment due to the cost of gold must be
410 accepted as inevitable, the gold can be recovered which makes this type of sorbent a
411 very attractive option for retaining elemental mercury during coal combustion without
412 producing toxic waste.
413
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418
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518 **Table 1.** Mercury retention by raw activated carbon (RB3) and activated carbon
519 impregnated with 5% gold (Au5-RB3) in different atmospheres.

Atmosphere	Hg retention ($mg\ g^{-1}$)	
	RB3	Au5-RB3
N_2	10[b]	2.0±0.2[a]
$6\%O_2 + 16\%CO_2 + 135 mgNm^{-3} SO_2 + 25\ mgNm^{-3} HCl + 100 mgNm^{-3}\ NO + N_2$	1.5±0.3	2.9±0.2[a]
$6\%O_2 + 16\%CO_2 + 135 mgNm^{-3} SO_2 + 25\ mgNm^{-3} HCl + 100 mgNm^{-3}\ NO + 3\%\ H_2O + N_2$	0.6±0.2	2.9±0.2[a]

520 [a] retention after 3 days, no saturation; [b]maximum retention capacity ($\mu g\ g^{-1}$)

521

522 **Table 2.** Preliminary analysis of costs

Initial investment	Cost ($)
Gold	92000
Support	3640
Reagents	1145
Cost of energy for preparing the sorbent	29000
Cost of installing the device	Not applicable
Operating costs for regeneration and maintenance	Not applicable
Total	125785

523

Figure captions

Figure 1. Schematic diagram of the experimental device used for the mercury retention and the thermal regeneration test.

Figure 2. Mercury adsorption curves of Au0.1-RB3 over three regeneration cycles under N_2 (a) and O_2+N_2 (b) atmospheres.

Figure 3. Mercury adsorption curves of Au5-RB3 over successive regeneration cycles under N_2 (a) and O_2+N_2 (b) atmospheres.

Figure 4. Diagram of the Au-Hg phase (data extracted from Okamoto and Massalski [23])

Figure 5. Mercury desorption curves for Au5-RB3 in repeated regeneration cycles under an N_2 atmosphere.

Figure 6. Mercury adsorption curves for Au5-RB3 over successive regeneration cycles under SO_2+N_2 (a) and HCl+N_2 (b) atmospheres.

Figure 7. Mercury adsorption curves for Au5-RB3 over repeated regeneration cycles under O_2+NO+SO_2+HCl+CO_2+H_2O+N_2 (a) and O_2+NO+SO_2+HCl+CO_2+N_2 (b) atmospheres.

Figure 8. Mercury desorption curves for Au5-RB3 in the first cycle of regeneration under N_2, O_2+NO+SO_2+HCl+CO_2+N_2 (SFG without H_2O) and O_2+NO+SO_2+HCl+CO_2+H_2O+N_2 (SFG) atmospheres.

Figure 9. Percentages of Hg^0 and Hg^{2+} in the different atmospheres studied.

Figure 10. Mercury speciation in the presence of RB3 (a) and Au5-RB3 (b) under N_2, O_2+NO+SO_2+HCl+CO_2+N_2 and O_2+NO+SO_2+HCl+CO_2+H_2O+N_2 atmospheres.

Figure 11. Image of the gold recovered.

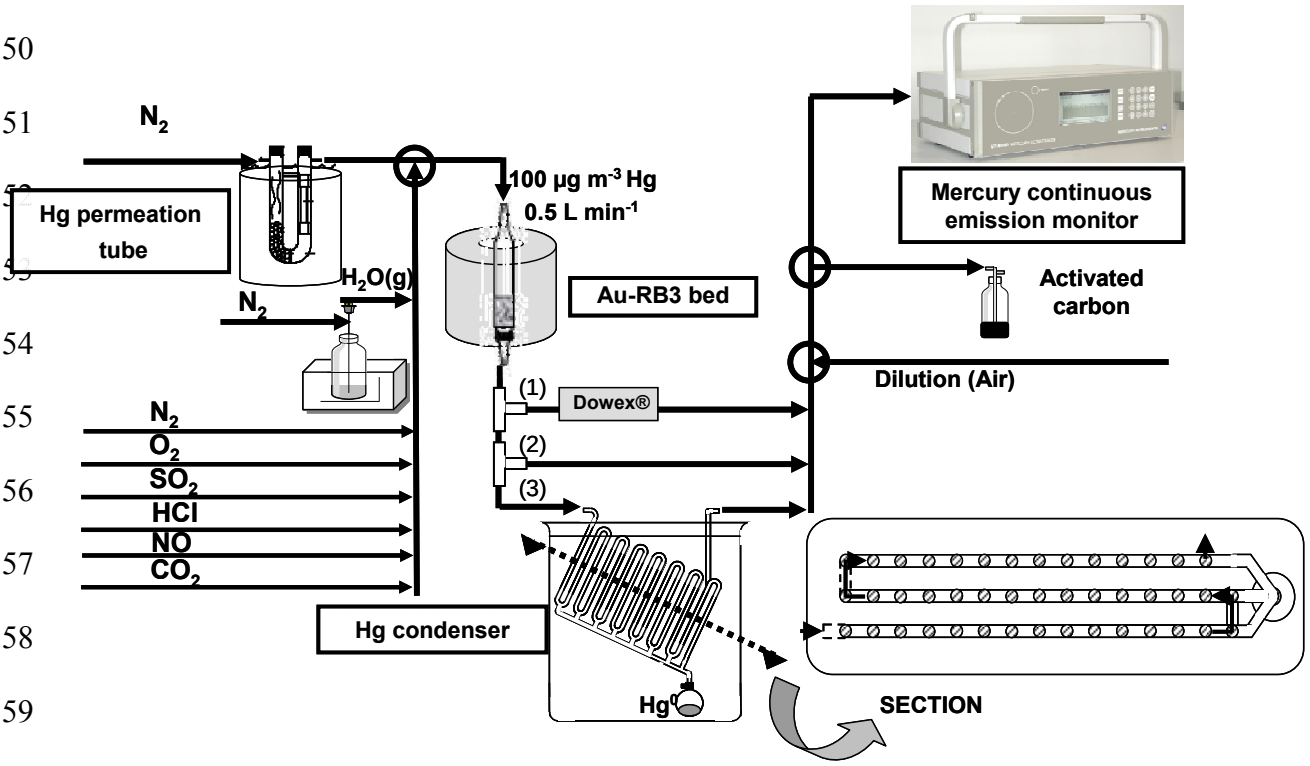


Figure 1

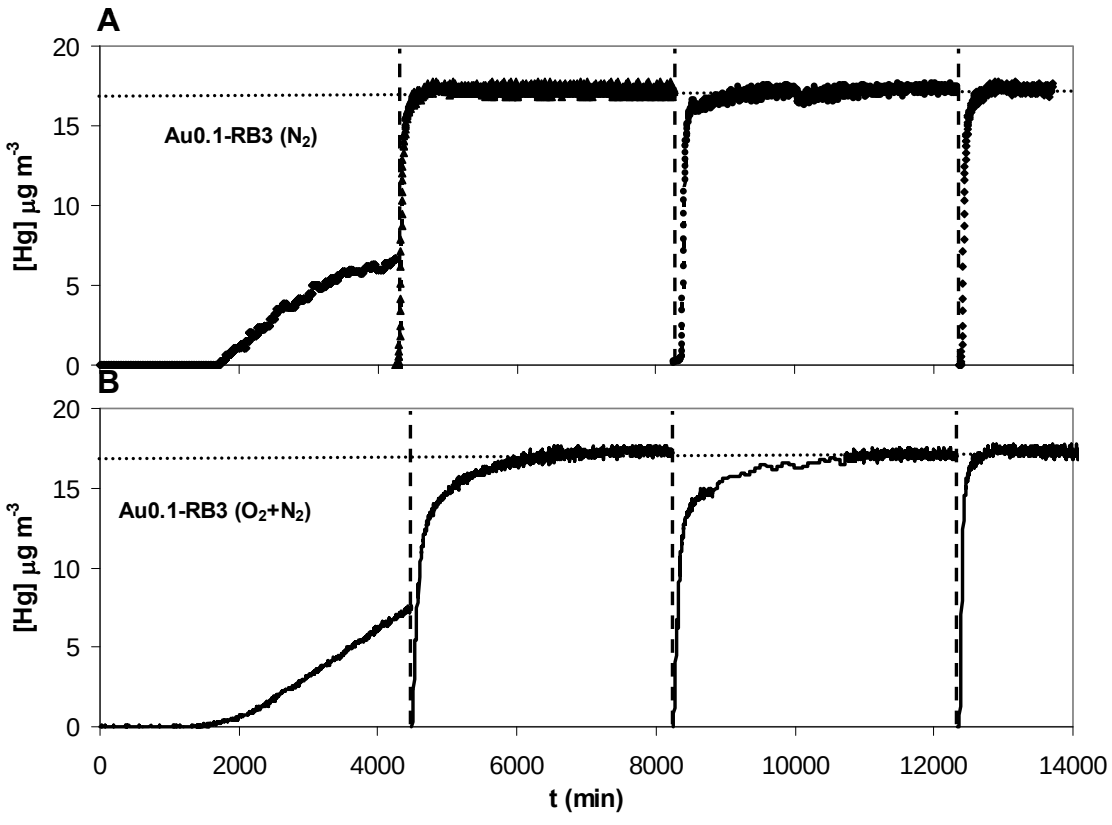
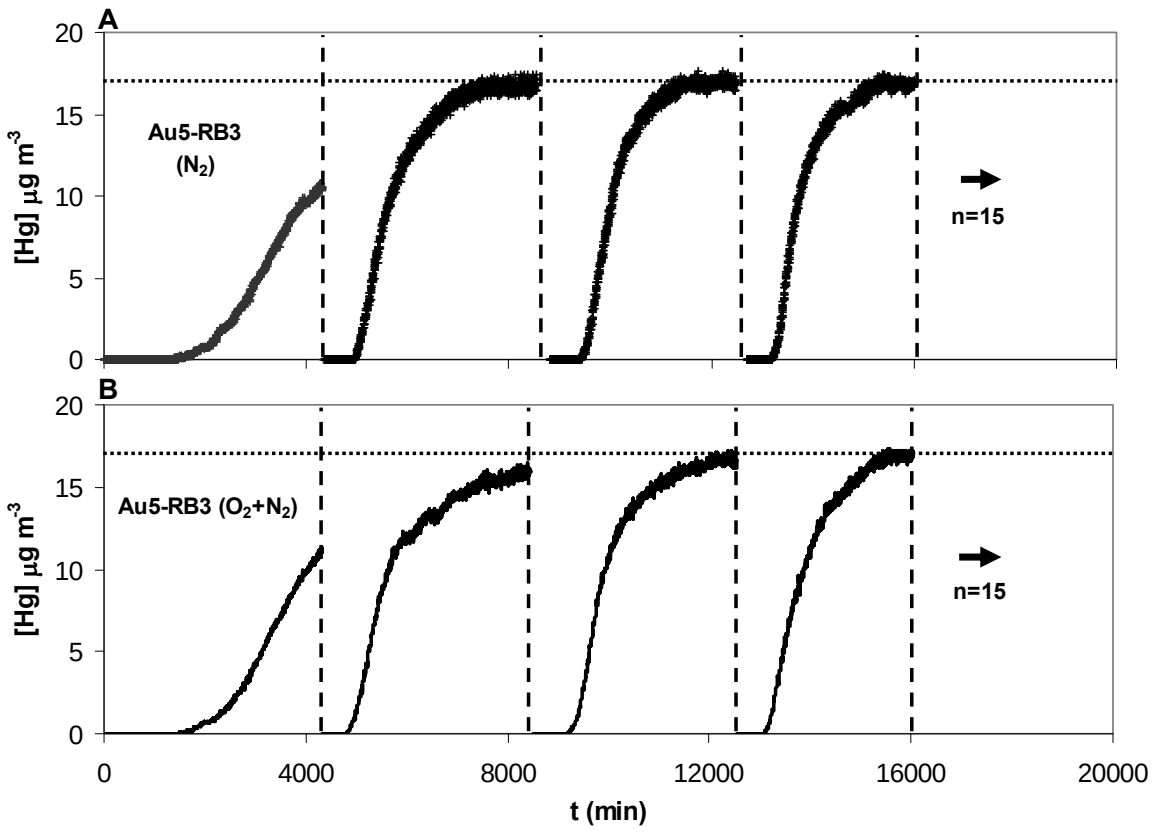


Figure 2



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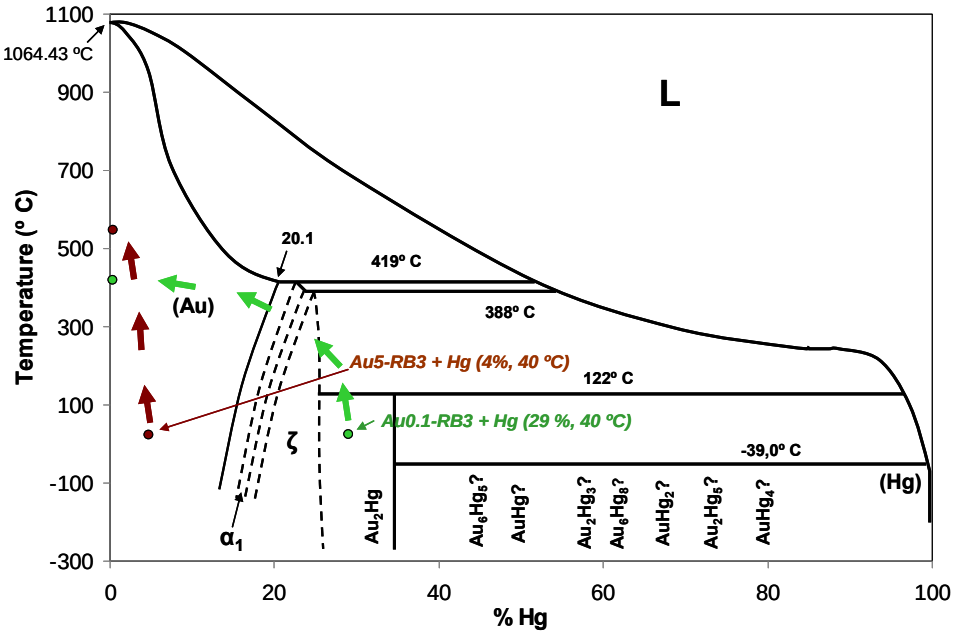

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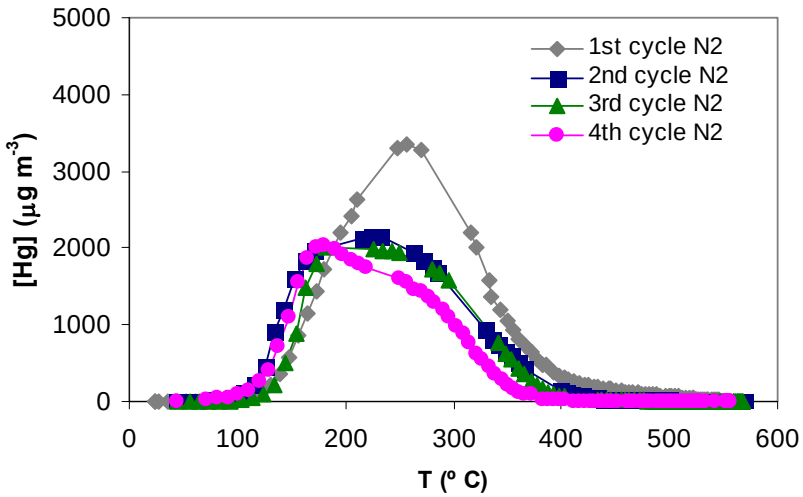

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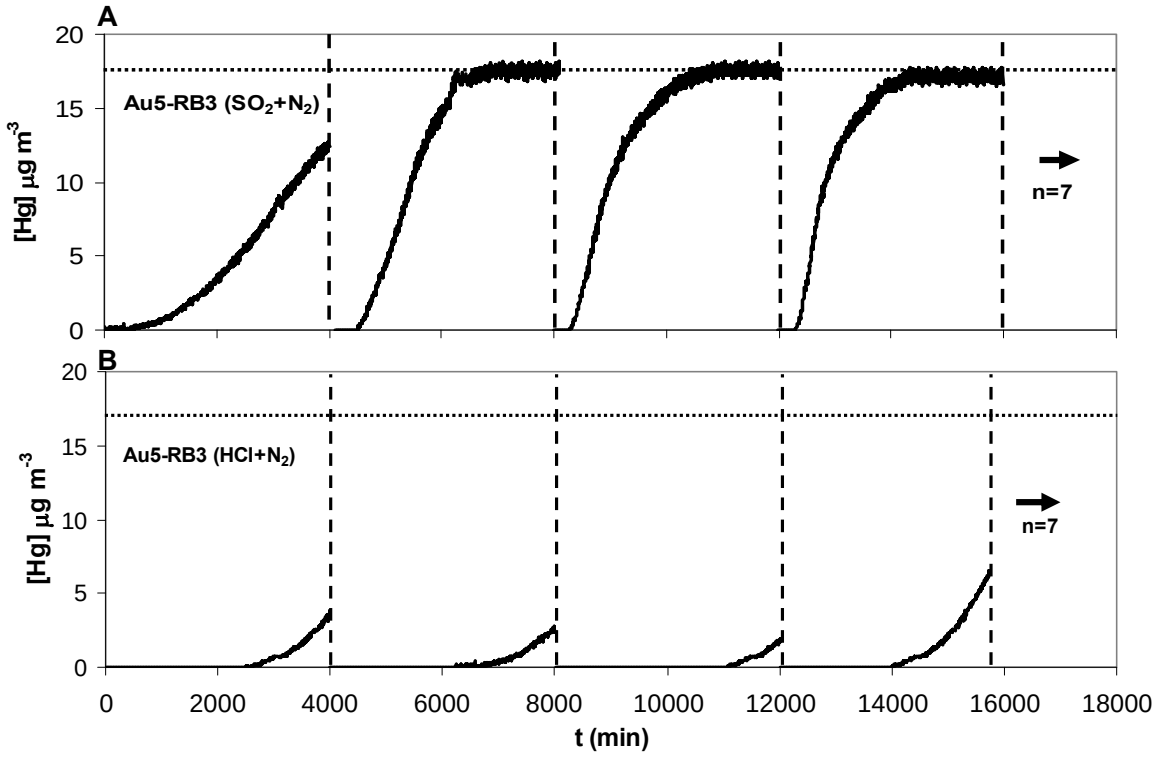

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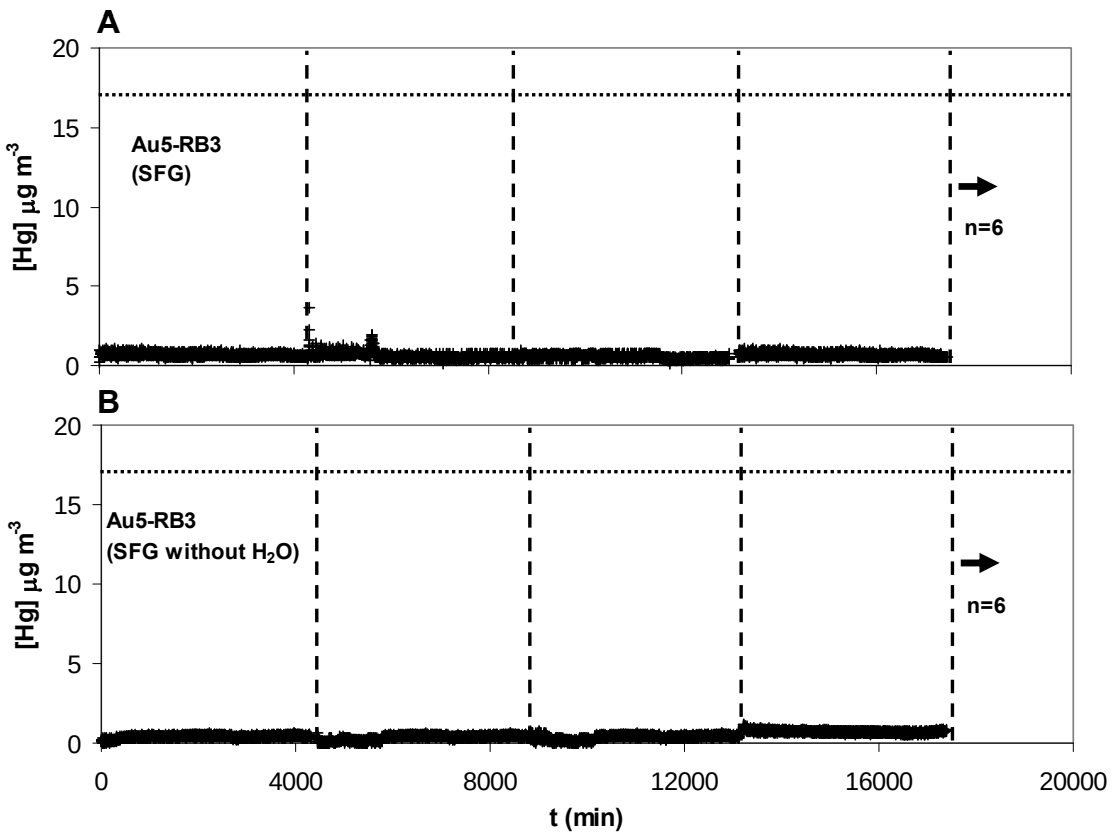


Figure 7

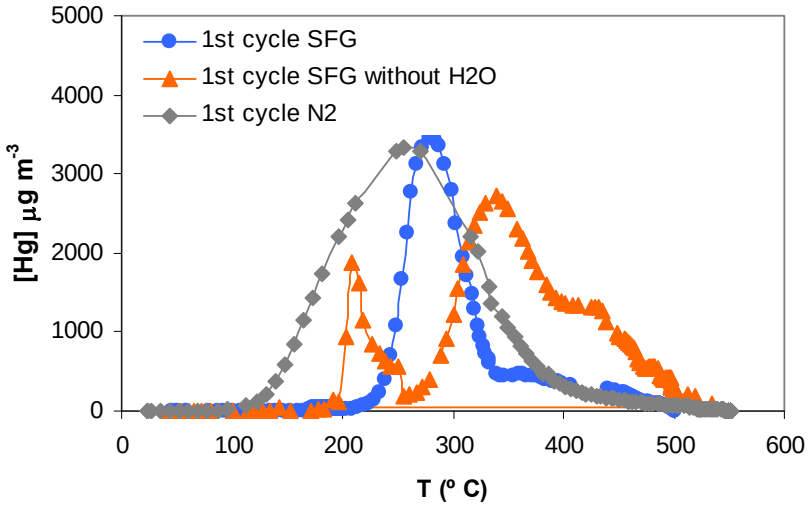


Figure 8

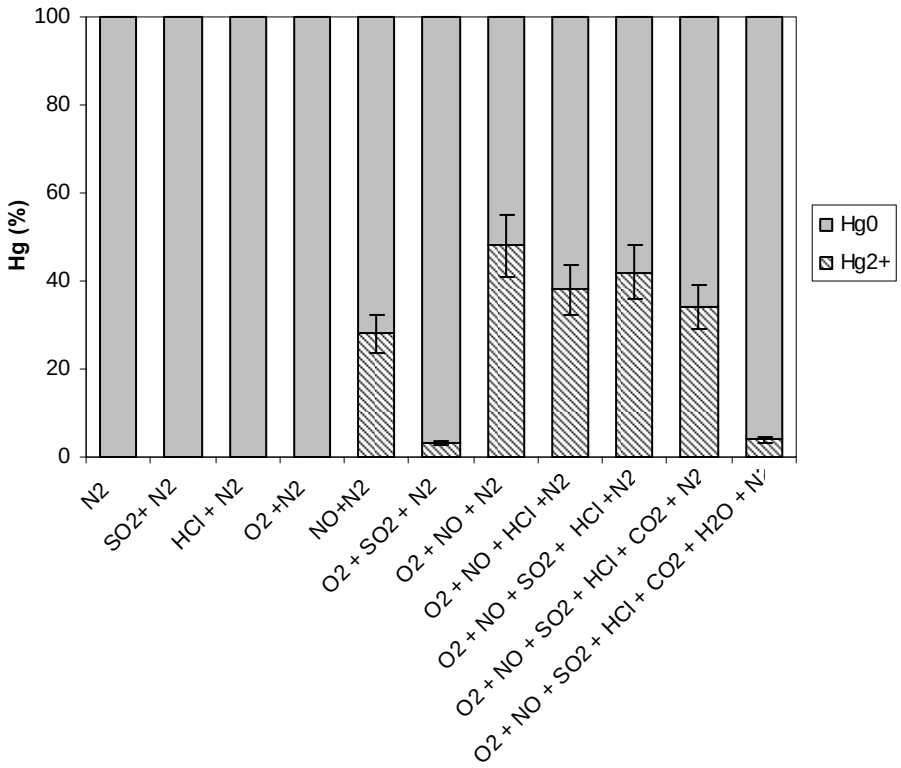

100
80
60
40
20
0
Hg (%)
Hg0
Hg2+
N2
SO2+ N2
HCl + N2
O2 +N2
NO+N2
O2 + SO2 + N2
O2 + NO + N2
O2 + NO + HCl +N2
O2 + NO + SO2 + HCl +N2
O2 + NO + SO2 + HCl + CO2 + N2
O2 + NO + SO2 + HCl + CO2 + H2O + N2

Figure 9

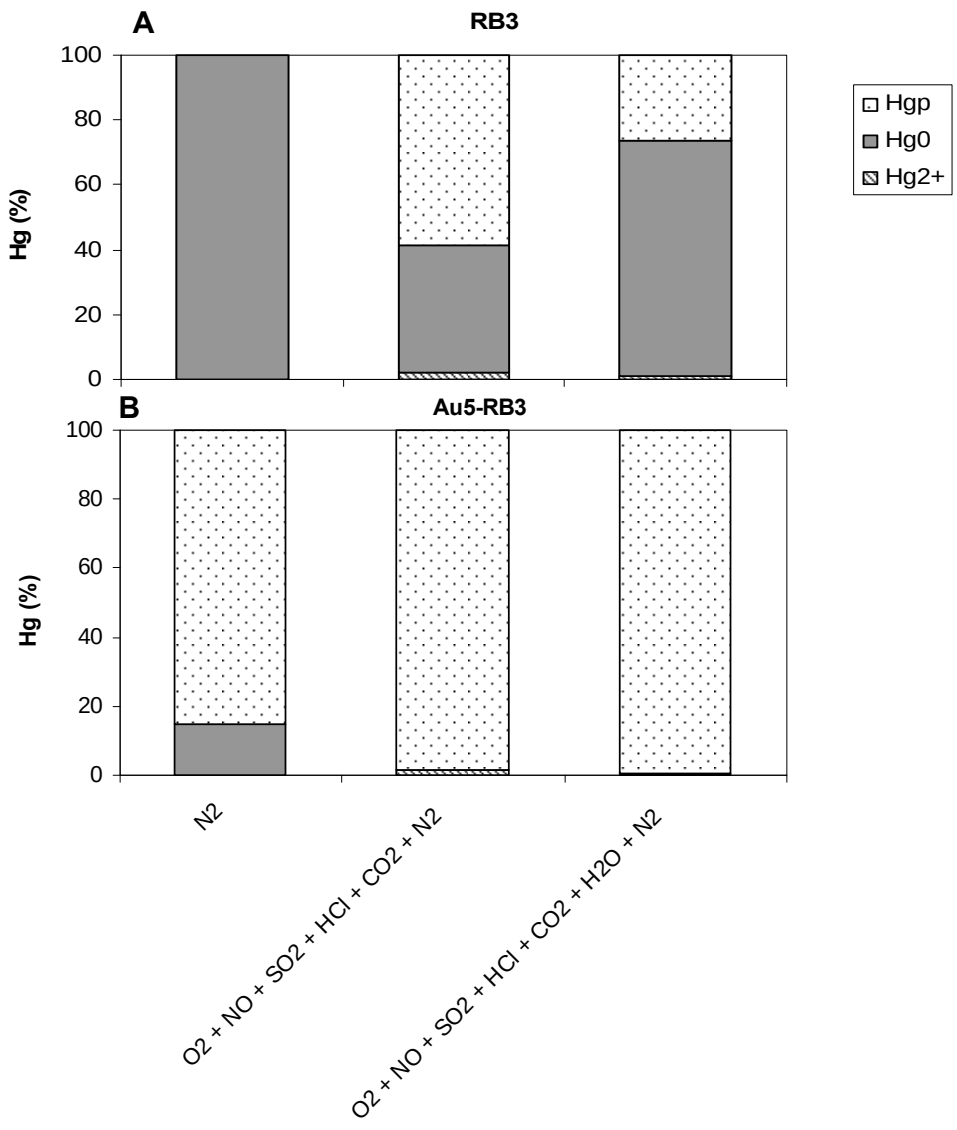
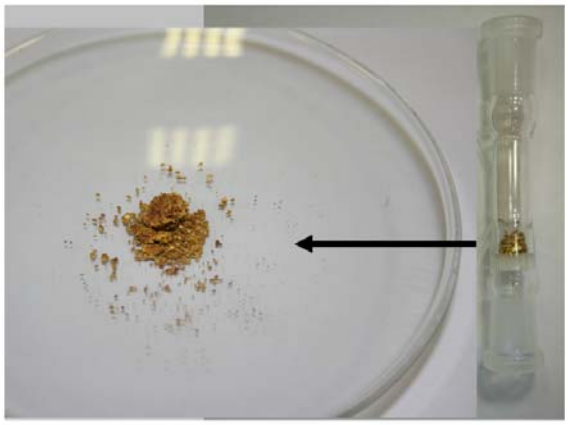

A
RB3
100
80
60
40
20
0
Hg (%)
Hgp
Hg0
Hg2+
B
Au5-RB3
100
80
60
40
20
0
Hg (%)
N2
O2 + NO + SO2 + HCl + CO2 + N2
O2 + NO + SO2 + HCl + CO2 + H2O + N2

Figure 10



661

662 Figure 11